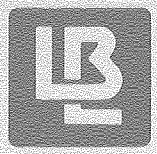

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CLUSTER-VARIATION METHOD FOR THE TRIANGULAR LATTICE GAS II. TRIANGLE APPROXIMATION

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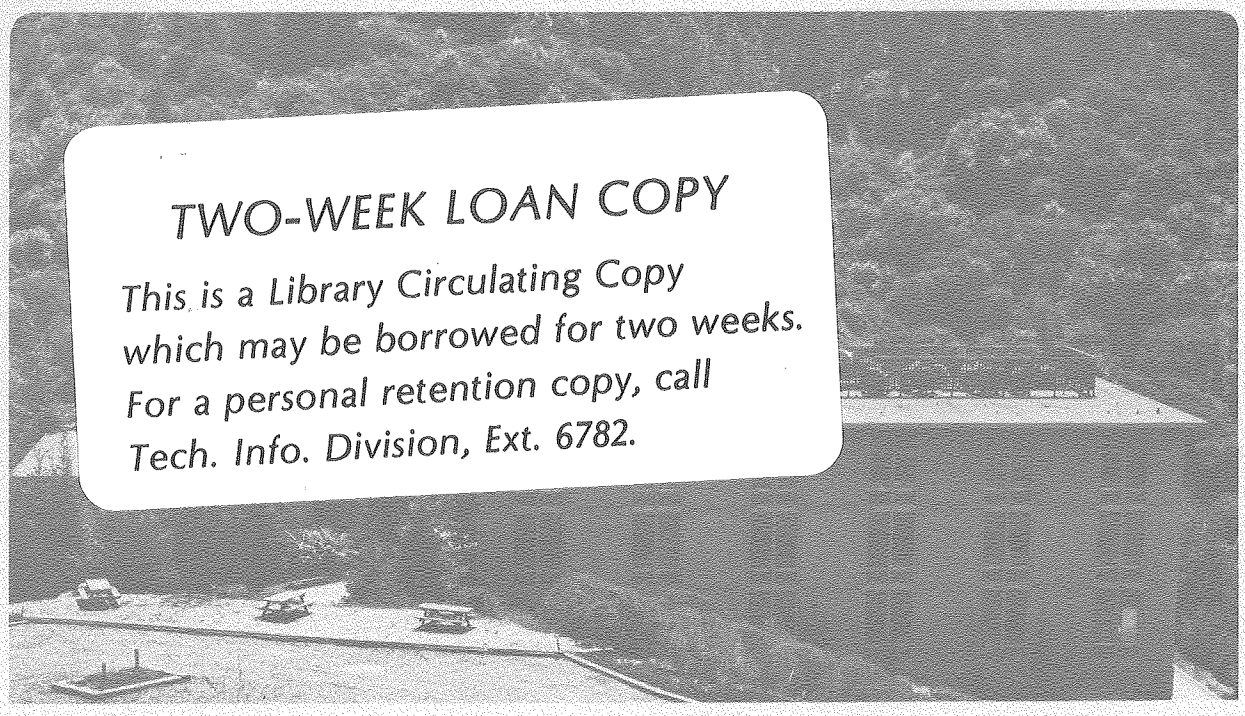
August 1980



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Cluster-variation method for the triangular lattice gas II. Triangle approximation

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A triangular lattice gas with nearest-neighbor repulsions and three-particle attractions is examined in a three-sublattice triangle approximation as a model for lithium intercalation in the transition metals dichalcogenides. Order-disorder phase diagrams and thermodynamic functions are computed. Peaks in the incremental capacity as function of concentration in the experimental data of Thompson are reproduced in our model.

1. INTRODUCTION

In the preceding [1] paper (hereafter referred to as I) the triangular lattice gas was investigated by a three-sublattice Bragg-Williams method as a model for the problem of lithium ordering in intercalated transition-metal dichalcogenides like TiS_2. The calculation of I illustrated qualitatively the origin of minima and maxima of the constant-temperature incremental capacity as a function of the concentration $\underline{x}$ in systems like Li_xTiS_2. In this paper a better approximation is used: it includes nearest-neighbor correlations between sites in a triangle cluster-variation calculation.

The cluster variation method has been developed by Kikuchi [2,3] as a hierarchy of self-consistent approximations for the combinational factors in the entropy of a lattice. The description of correlations between lattice sites is limited by the size of the chosen basic cluster, while long-range order can be introduced by dividing the lattice into a number of sublattices consistent with the ground state.

For the triangular lattice with three sublattices and nearest-neighbor repulsion only, the point approximation was examined in I. The pair approximation is equivalent to the Bethe-Peierls method and has been applied to the triangular lattice with repulsive nearest-neighbor and attractive second-nearest-neighbor interactions by Campbell and Schick [4]. Because of its "one-dimensional" characteristics, however, this model leads to paradoxical results, like negative entropies

close to the concentration $\underline{x} = 1/2$ at low temperatures. Another failure, apparent in all closed-packed lattices, is that the Bethe-Peierls method gives wrong results for the energy at zero temperature: the probability of existence of nearest-neighbor pairs of particles is zero for $\underline{x} \leq 1/2$, while, as discussed in I, the correct result is finite for $\underline{x} > 1/3$. We therefore choose not to apply the pair approximation to the present problem.

We define as our basic cluster a closed triangle containing nearest-neighbor points belonging to the three different sublattices defined in I. This approximation was first used by Burley [5] to study antiferromagnetic behavior in an Ising model, which has been proved by Yang and Lee [6] to be equivalent to our lattice gas problem. While Burley assumed the distribution of spins on two of the sublattices to be equal, we give here a more general solution, including the possibility of three different site occupancies. Furthermore, we incorporate interactions between three particles in the model. This is necessary to remove the artificial symmetry about $\underline{x} = 0.5$ found in the phase diagram of I. We thus have here two adjustable parameters, namely the temperature and the three-body potential.

Our cluster-variation calculation is presented in Section 2 and the Appendix. The resulting phase diagrams are shown in Section 3, while the behavior of the entropy and the incremental capacity is the subject of Section 4. The results are discussed further and conclusions presented in Section 5.

2. THE CLUSTER-VARIATION CALCULATION

To each lattice site we associate a number $\underline{i}$ such that $i = 0$ if the site is empty and $i = 1$ if the site is occupied. Accordingly, we define the point probabilities x_i^ν for the $\underline{i}$ state of a point in the sublattice ν ($\nu = \alpha$, β or γ). In the notation of I, $x_i^\nu = n_\nu$. The probability for an $\underline{i}$ - $\underline{j}$ bond (where $\underline{i},\underline{j} = 0$ or 1) between nearest-neighbor sites on the sublattices ν and ν' is denoted by $y_{ij}^{\nu\nu'}$. Finally the probability for an $\underline{i}$ - $\underline{j}$ - $\underline{k}$ configuration on an equilateral nearest-neighbor triangle containing points on the sublattices α, β and γ, in this order, is denoted by z_{ijk}. The following relations hold between the configuration probabilities for the different clusters:

$$\sum_{ijk} z_{ijk} = 1 \tag{2.1a}$$

$$y_{ij}^{\alpha\beta} = \sum_k z_{ijk} \; ; \qquad y_{jk}^{\beta\alpha} = \sum_i z_{ijk} \; ; \qquad y_{ki}^{\gamma\alpha} = \sum_j z_{ijk} \; ; \tag{2.1b}$$

$$x_i^\alpha = \sum_{jk} z_{ijk} \; ; \qquad x_j^\beta = \sum_{ik} z_{ijk} \; ; \qquad x_k^\gamma = \sum_{ij} z_{ijk} \; . \tag{2.1c}$$

We assume the particles to interact through a nearest-neighbor repulsion $\underline{U}$ (as in I) and we add the value $\underline{U}\phi$ for each closed nearest-neighbor triangle of particles. We take ϕ to be negative to simulate the decreasing degree of ionization of the Li atoms in Li_xTiS_2 as $\underline{x}$ increases. Nuclear-magnetic-resonance data [7] suggest that, while the ionization is essen-

tially complete at small $\underline{x}$, 10 to 20% of an electron remains in the neighborhood of a Li atom at $\underline{x} = 1$. Simple electrostatic arguments then suggest that ϕ takes values between (-0.3) and (-0.55). The energy of the lattice gas with $\underline{N}$ sites is written as

$$E = NU\ (y_{11}^{\alpha\beta} + y_{11}^{\beta\gamma} + y_{11}^{\gamma\alpha} + 2\phi\ z_{111}). \qquad (2.2)$$

Ground-state structures are found by minimizing this energy with respect to the variables $\{z_{ijk}\}$, subject to the constraint of Eq. (2.1a) and an additional relation obtained from a well-determined concentration:

$$x = \frac{1}{3}\ (x_1^{\alpha} + x_1^{\beta} + x_1^{\gamma}). \qquad (2.3)$$

This is a typical problem of linear programming [8]. Ordered structures, corresponding to discontinuities in $(\partial E/\partial x)$, result at $\underline{x} = 1/3$ and $2/3$, as in I, for $\phi > -1/2$. The structure at $\underline{x} = 2/3$ disappears for $\phi < -1/2$; the one at $\underline{x} = 1/3$ for $\phi < -3/2$: then the separation of all available particles into a phase of completely filled sites coexisting with a phase of empty sites becomes energetically favorable.

The configurational entropy can be generalized from Kikuchi's equation [2] for the one-sublattice triangular lattice in a straightforward way and is written as

$$S = k_B \ln \frac{\prod_{ij} \left(Ny_{ij}^{\alpha\beta}\right)! \left(Ny_{ij}^{\beta\gamma}\right)! \left(Ny_{ij}^{\gamma\alpha}\right)!}{\left[\prod_{ijk} (Nz_{ijk})!\right]^2 \prod_{\nu} \prod_{i} \left[(N x_i^{\nu})!\right]^{1/3}} . \tag{2.4}$$

The grand potential can then be expressed in the notation of I as

$$\begin{aligned} \omega = & y_{11}^{\alpha\beta} + y_{11}^{\beta\gamma} + y_{11}^{\gamma\alpha} + 2\phi\, z_{111} \\ & + \tau \Big\{ 2 \sum_{ijk} L(z_{ijk}) \\ & - \sum_{ij} L(y_{ij}^{\alpha\beta}) - \sum_{jk} L(y_{jk}^{\beta\gamma}) - \sum_{ki} L(y_{ki}^{\gamma\alpha}) \\ & + 1/3 \Big[\sum_{i} L(x_i^{\alpha}) + \sum_{j} L(x_j^{\beta}) + \sum_{k} L(x_k^{\gamma}) \Big] \Big\} \\ & - \tfrac{1}{3}\mu \left(x_1^{\alpha} + x_1^{\beta} + x_1^{\gamma}\right) , \end{aligned} \tag{2.5}$$

where the operator L, defined as

$$L(u) = u (\ln u - 1), \tag{2.6}$$

results from using Stirling's approximation in Eq. (2.4). The eight triangle configuration probabilities z_{ijk} are taken as independent variables for the minimization of ω, for given μ, τ and ϕ. The normalization constraint of Eq. (2.1a) is introduced through a Lagrange multiplier. Kikuchi's "Natural iteration" [9] method was used in the minimization procedure, which is described in the Appendix.

3. PHASE DIAGRAMS

We define the regions (3), (12), (21) and (111) in the (x,τ) phase diagram as in I. For $\phi = 0$, the particle-hole symmetry discussed in I holds and the (21) phase is the mirror image of the (12) phase about $x = 1/2$. This phase diagram is shown in Figure 1. Comparing this with the Bragg-Williams phase diagram of I we notice two qualitative differences: (a) the cluster-variation phase diagram shows a valley at $x = 1/2$ and (b) the disordered phase (3) continues to exist at $\tau = 0$. This topological evolution of the phase diagram as the approximation is improved parallels that for the fcc binary alloy [10].

For the first effect, we should notice that Wannier [11] has solved exactly the zero-field Ising antiferromagnet, and obtained a disordered stable phase. Our order-disorder coexistence region, which extends near $x = 1/2$ down to $\tau = 0.25$, should, with better approximations, continue to lower temperatures and include the $x = 1/2$, $\tau = 0$ point. The triangle cluster approximation, though better than the "point" approximation, still seems to be unreliable around $x = 1/2$ at low temperatures. The difference between the free energies of the different phases is very small in this region and the (111) phase happens to have a higher entropy.

The zero-temperature limit is usually avoided in cluster-variation calculations. Van Baal [12] justifies this practice with the argument that the approximations used in the description of the energy, which is the predominant part of the free

energy at low temperatures, makes the model lose contact with reality in this limit. We find the zero-temperature behavior to be of theoretical interest, however, to confirm the existence of the ground-state structures that led to the division of the lattice into sublattices. Our results show that the concentrations $x = 1/3$ and $2/3$ at $\tau = 0$ are second-order transition points between the phase (111) and the phases (12) and (21), respectively. For $x < 1/3$, the phases (3) and (12) have the same energy. The short-range correlations included in the cluster description allow for the existence of a disordered phase with zero energy at low concentrations. The intervals where each phase predominates are determined by the zero-temperature-limit entropies. The phases (3) and (12) coexist between $x = 0.2280$ and $x = 0.2515$. This interval corresponds to the first-order phase transition occuring in the lattice gas with infinite nearest-neighbor repulsion, treated by Burley [13].

In Figure 2, the phase diagram for $\phi = -0.3$ illustrates the asymmetry introduced by interactions between more than two particles. The region of existence of the (21) phase is significantly reduced, although the zero-temperature behavior remains the same as for $\phi = 0$. Below $\phi = -0.5$, however, the (21) phase and the ordered structure at $x = 2/3$ disappear altogether as discussed in Section 2. Such a behavior is displayed in the phase diagram of Figure 3, for $\phi = -0.6$. As $\tau \to 0$, the interval of coexistence between the phases (12) and (3) extends to the whole interval between $x = 1/3$ and $x = 1$.

4. THERMODYNAMIC FUNCTIONS

We discuss the behavior of the reduced entropy,

$$s = S/(Nk_\beta) \ , \tag{4.1}$$

and the reduced incremental capacity, defined in I, and compare the latter to experimental results for systems like Li_xTiS_2.

The entropy at fixed temperature as a function of the concentration shows minima at small τ where ordered structures occur. The negative three-particle potential increases the values of the entropy for $x > 1/2$. These two effects are illustrated in Figure 4, where results are presented for several temperatures at $\phi = -0.3$, which corresponds to an ionization of 90% at $x = 1$.

In regards to the incremental capacity, our results also show minima at concentrations where ordered structures are expected, as in I. We are able to account also for the peaks in the experimental data [14] for Li_xTiS_2 at $x = 1/9$ and $1/4$. For any ϕ and $\tau < 0.2$ a smooth maximum appears near $x = 1/9$. The point $x = 1/4$ is inside the small interval where a diverging incremental capacity indicates an order-disorder transition. A smooth maximum near $x = 6/7$ can be reproduced for $\phi = -0.3$, $\tau = 0.2$. The negative three-particle interaction produces high values for the incremental capacity in the disordered phase for $x > 1/2$. In Figure 5, results

are presented for $\phi = -0.3$ and several temperatures, together with Thompson's results [14] for Li_xTiS_2, where the mentioned peaks are observed, and for $Li_x\ Ta_{0.8}\ Ti_{0.2}\ S_2$, where minima at $x = 1/3$ and $2/3$ occur [15].

A nearest-neighbor approximation in a triangular lattice gas can thus account semi-quantitatively for the experimental features in the incremental capacity for lithium intercalation in some transition-metal dichalcogenides. We should mention that a cluster-variation calculation cannot predict the correct analytical behavior of thermodynamic functions at critical points, although their location in the phase diagram can be predicted with a satisfactory accuracy.

5. CONCLUSIONS

We have presented here order-disorder phase diagrams for the triangular lattice gas with nearest-neighbor pairwise repulsive and three-particle attractive interactions. The main effect of the three-particle parameter is to decrease the temperature range of existence of the ordered phase corresponding to the structure at $x = 2/3$, thus removing the particle-hole symmetry found in I. This is reflected in the curves for the entropy and the incremental capacity as functions of the concentration. The qualitative picture given in I for the minima and maxima of the incremental capacity is confirmed. Furthermore, we are able to reproduce

quantitatively the position of maxima and minima of the experimental data.

We thus confirm the validity of the lattice gas model as a first approximation for the problem of ordering of Li^+ ions in systems like Li_xTiS_2. Better results can almost certainly be achieved by introducing longer-range interactions. The improvements, however, will be limited mainly by the inaccurate description of the guest-host interaction and the electronic contributions due to the filling of the TiS_2 conduction band.

ACKNOWLEDGEMENTS

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APPENDIX

We describe here the "natural interation" scheme used to minimize Eq. (2.5), given μ, τ and ϕ. We define

$$\omega_o = \omega + \lambda \left(1 - \sum_{ijk} z_{ijk} \right) , \tag{A.1}$$

where the Lagrange multiplier λ was used to introduce the constraint of Eq. (2.1a). The equations

$$\frac{\partial \omega_o}{\partial z_{ijk}} = 0 \tag{A.2}$$

lead to the superposition expression

$$z_{ijk} = \exp[(\lambda + \mu\, n_{ijk} - \varepsilon_{ijk})/2\tau]\; Y_{ijk}^{1/2}\; X_{ijk}^{-1/6} , \tag{A.3}$$

where for the $\underline{i}$-$\underline{j}$-$\underline{k}$ triangle configuration we defined the number of particles per lattice site

$$n_{ijk} = \frac{1}{3} (\delta_{i_1} + \delta_{j_1} + \delta_{k_1}) , \tag{A.4}$$

the energy in units of $\underline{U}$ per lattice site

$$\varepsilon_{ijk} = \delta_{i_1}\, \delta_{j_1} + \delta_{j_1}\, \delta_{k_1} + \delta_{k_1}\, \delta_{i_1}$$

$$+ 2\phi\; \delta_{i_1}\, \delta_{j_1}\, \delta_{k_1} \tag{A.5}$$

(where δ_{mn} is Kronecker's delta) and the quantities

$$Y_{ijk} = y_{ij}^{\alpha\beta}\, y_{jk}^{\beta\gamma}\, y_{ki}^{\gamma\alpha} \tag{A.6}$$

and

$$X_{ijk} = x_i^{\alpha}\, x_j^{\beta}\, x_k^{\gamma} \quad . \tag{A.7}$$

In Eq. (A.3) the triangle probabilities are expressed as products of (a) the probabilities for the smaller clusters, (b) a Gibbs factor and (c) a normalization factor $\exp(\lambda/2\tau)$. The Lagrange multiplier λ can be identified with the minimized grand potential, through the relation

$$\omega_o \equiv \omega_o - \sum_{ijk} z_{ijk} \frac{\delta\omega_o}{\delta z_{ijk}} = \lambda \quad . \tag{A.8}$$

The normalization relation of Eq. (2.1a) gives a cluster-variation approximation for the grand partition function Z as a sum over the triangle cluster, the Gibbs factor being weighted by the configuration probabilities of pairs and points, in the form

$$Z^{1/2N} = \exp(-\lambda/2\tau) = \sum_{ijk} \exp[(\mu n_{ijk} - \epsilon_{ijk})/2\tau] \times Y_{ijk}^{1/2}\, X_{ijk}^{-1/6} . \tag{A.9}$$

The natural iteration calculation proceeds in the following steps: (a) initial values are chosen for the point and

the pair variables (e.g., $x_1^{\alpha} = 0.8$, $x_1^{\beta} = 0.5$, $x_1^{\gamma} = 0.2$ for the ordered phases, and $x_1^{\alpha} = x_1^{\beta} = x_1^{\gamma} = 0.5$ for the disordered phase; $y_{ij}^{\alpha\beta} = x_i^{\alpha} x_j^{\beta}$ etc.); (b) a value of λ results from Eq. (A.9); (c) corresponding values for the set of triangle clusters $\{z_{ijk}\}$ are obtained from Eq. (A.3); (d) new values for $\{x_i^{\nu}\}$ and $\{y_{ij}^{\nu\nu'}\}$ are derived through the summation rules of Eq. (2.1b) and (2.1c); (e) steps (b)-(d) are repeated until a convergence criterion is satisfied.

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FIGURE CAPTIONS

Figure 1 Phase diagram in the (x,τ) plane for the triangular lattice gas in the triangle approximation with nearest-neighbor repulsions only.

Figure 2 Phase diagram in the (x,τ) plane for the t iangle lattice gas with a three-particle parameter $\phi = -0.3$. Horizontal lines are drawn for $\tau = 0.1$, 0.2 and 0.3 so that the behavior of the constant-temperature parameters of Figure 4 can be compared with the phase diagram.

Figure 3 Phase diagram in the (x,τ) plane for the triangular lattice gas with a three-particle parameter $\phi = 0.6$.

Figure 4 Reduced entropy and molar entropy (in J. mol $^{-1}$. K^{-1}) as functions of concentration for a three-particle parameter $\phi = -0.3$ and several values of the reduced temperature τ. Arrows indicate second-order transition points for $\tau = 0.1$. This Figure corresponds to the phase diagram of Figure 2.

Figure 5 Reduced incremental capacity multiplied by the reduced temperature ($\tau \cdot \partial x/\partial \mu$) and incremental capacity (in volts $^{-1}$ assuming T = 300K) for $\phi = -0.3$ and (a) $\tau = 0.1$, (b) $\tau = 0.2$, (c) $\tau = 0.3$, (d) $\tau = 0.4$ and the experimental results for (e) Li_xTiS_2 and (f) $Li_x\ Ta_{0.8}\ Ti_{0.2}\ S_2$ from Reference 15. In (a) arrows indicate second-order transition points.

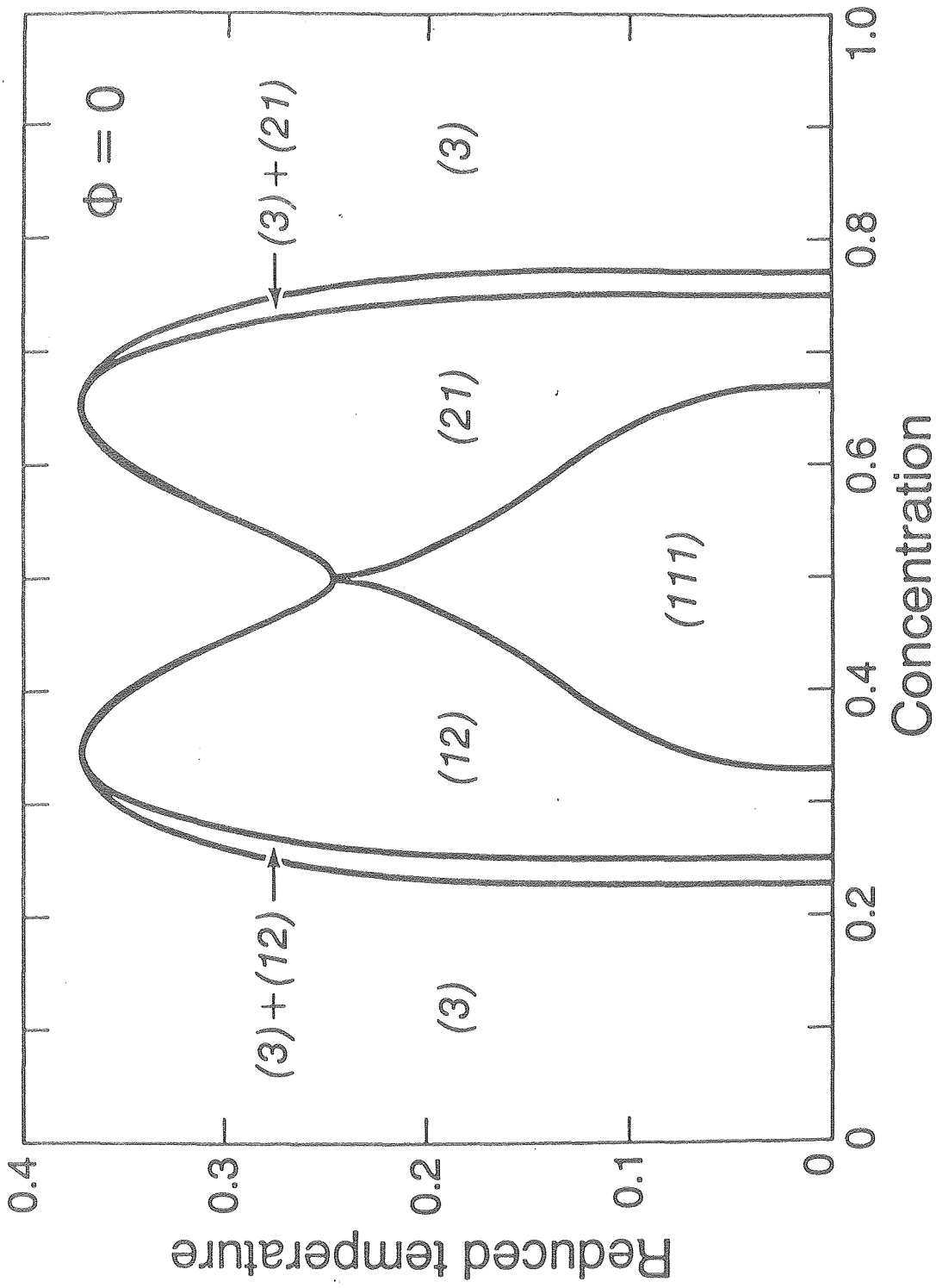
Reduced temperature
Concentration
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
$\Phi = 0$
(3) + (21)
(3) + (12)
(3)
(3)
(21)
(12)
(111)

Figure 1

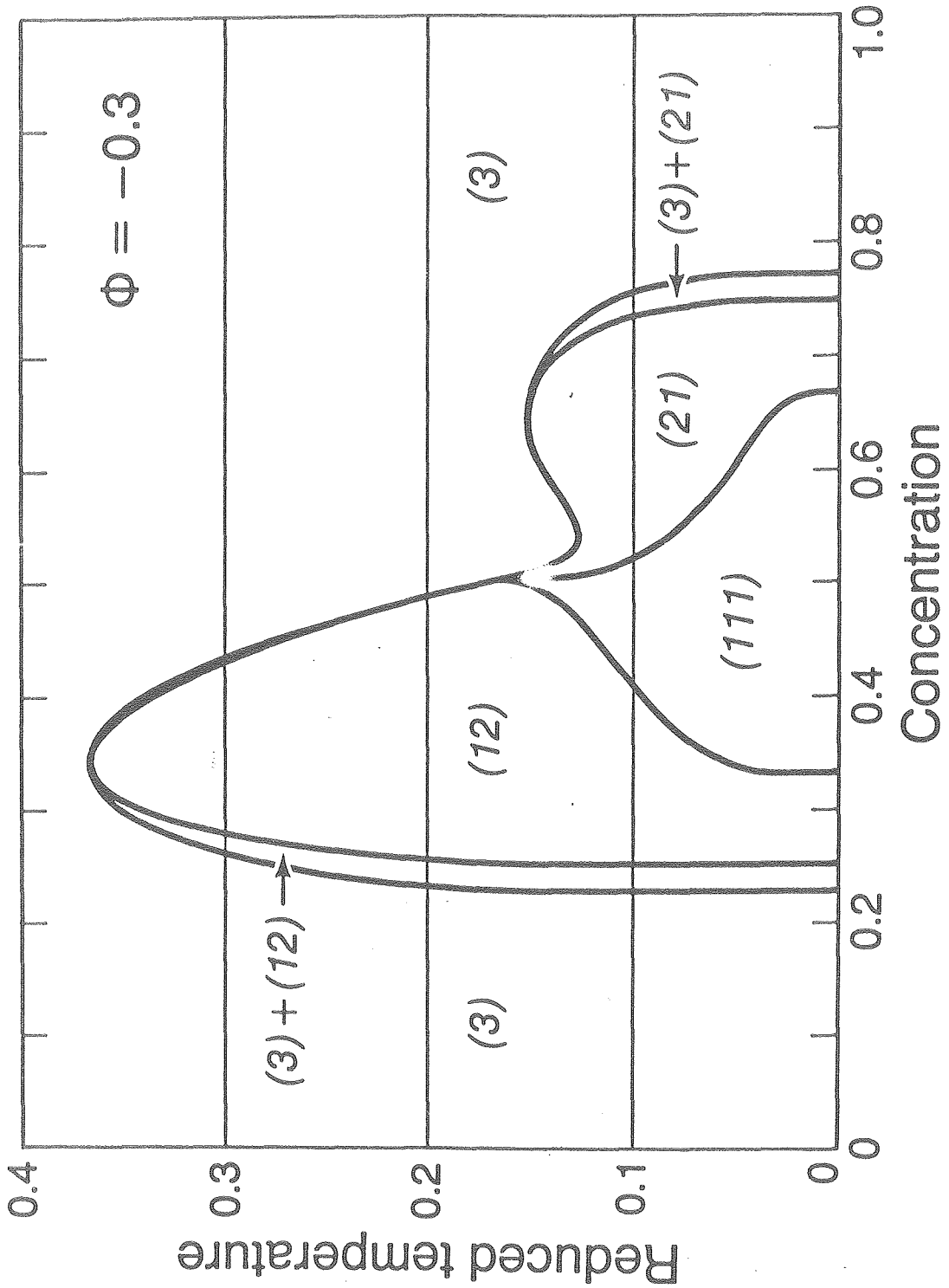
Φ = −0.3
(3)
(12)
(111)
(21)
(3)+(21)
(3)+(12)
(3)
Reduced temperature
Concentration
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
1.0

Figure 2

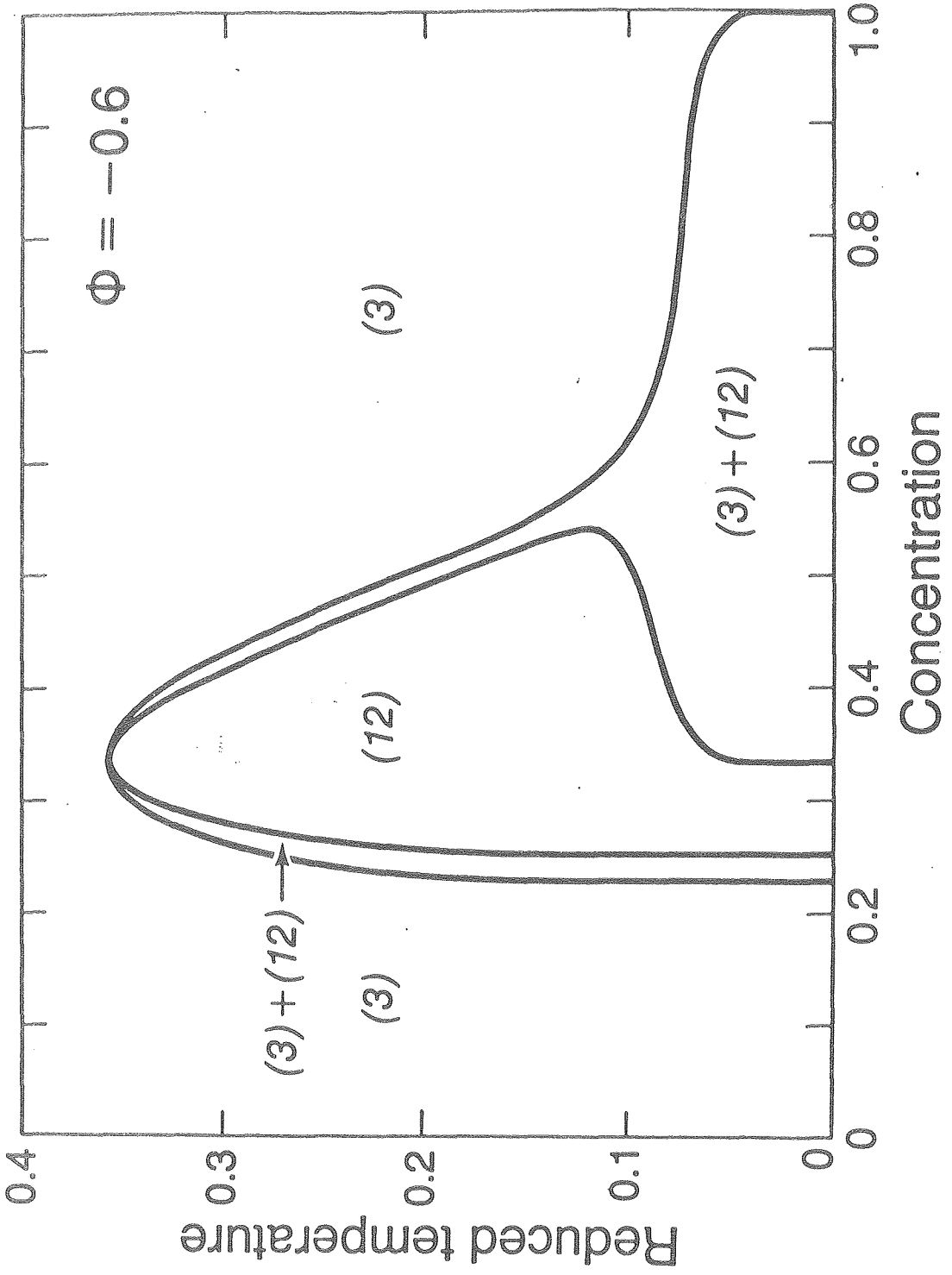
Φ = −0.6
(3)
(12)
(3)
(3) + (12)
(3) + (12)
Reduced temperature
Concentration
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0

Figure 3

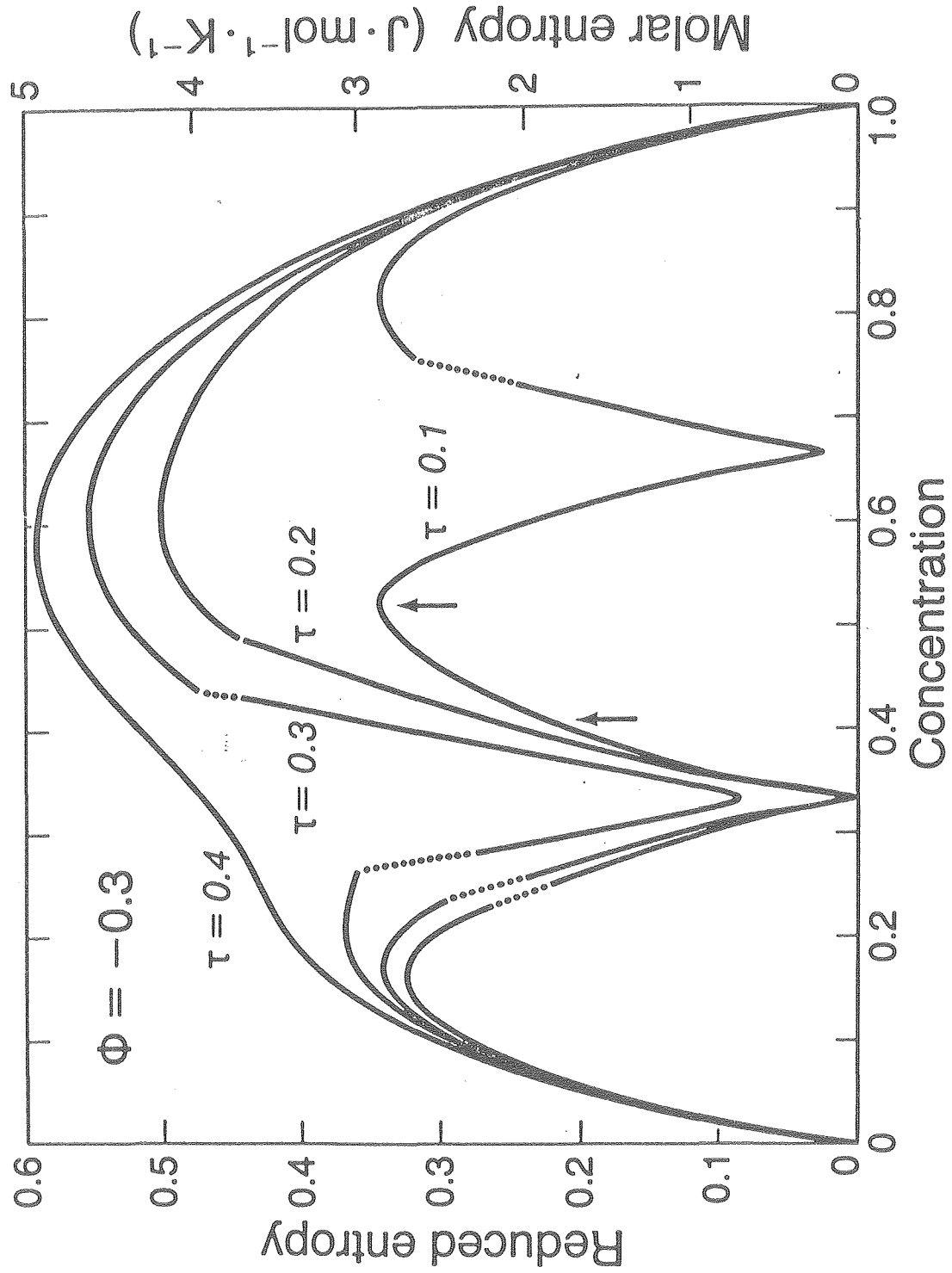
Reduced entropy
Molar entropy (J · mol⁻¹ · K⁻¹)
Concentration
Φ = −0.3
τ = 0.4
τ = 0.3
τ = 0.2
τ = 0.1
0.6
0.5
0.4
0.3
0.2
0.1
0
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0

Figure 4

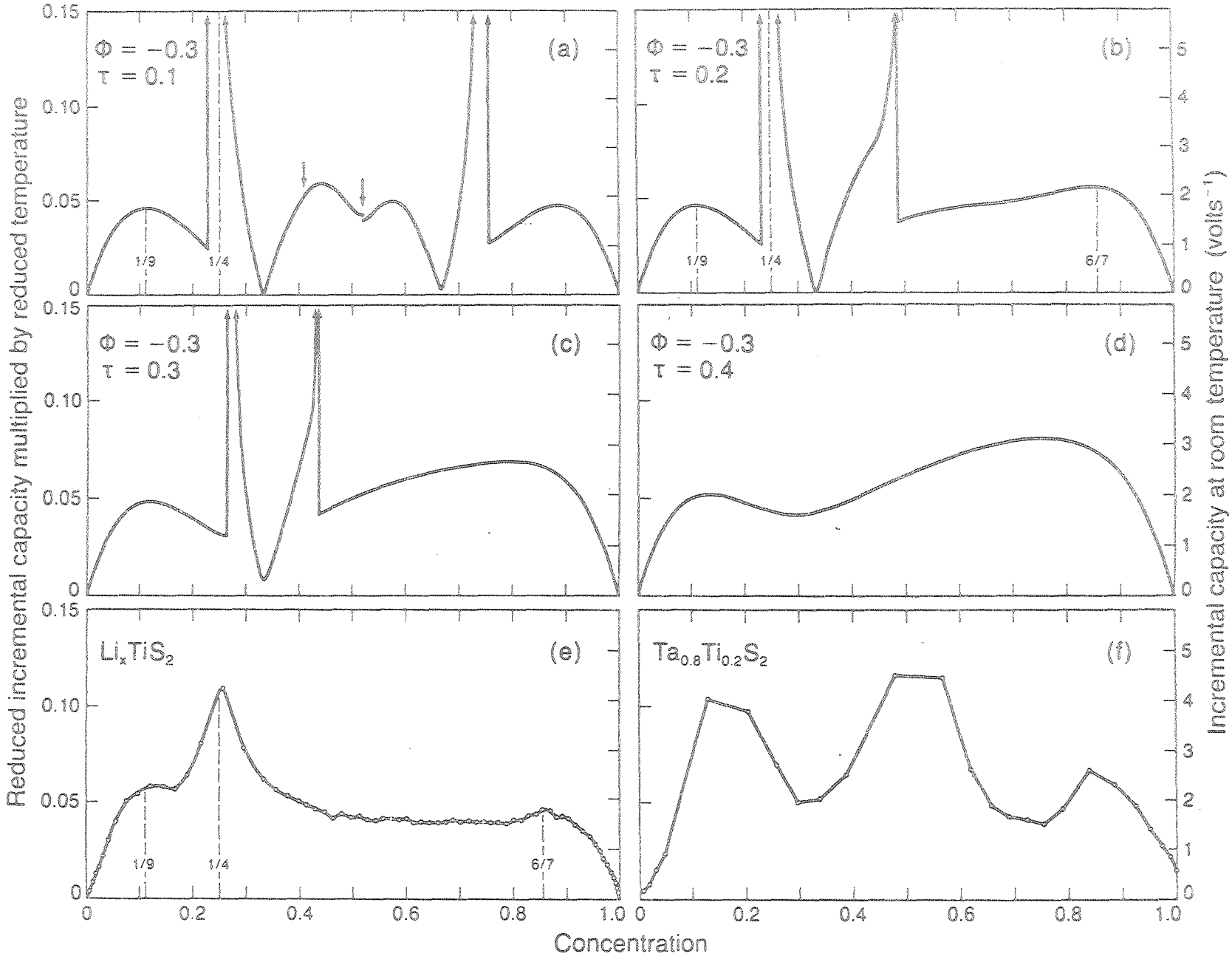
Φ = −0.3
τ = 0.1
(a)
Φ = −0.3
τ = 0.2
(b)
Φ = −0.3
τ = 0.3
(c)
Φ = −0.3
τ = 0.4
(d)
Li_xTiS_2
(e)
$Ta_{0.8}Ti_{0.2}S_2$
(f)
1/9
1/4
6/7
Reduced incremental capacity multiplied by reduced temperature
Incremental capacity at room temperature (volts^{-1})
Concentration
0
0.05
0.10
0.15
0.2
0.4
0.6
0.8
1.0
1
2
3
4
5

Figure 5